

09/628,623

PCT

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International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08L 67/02		A1	(11) International Publication Number: WO 97/15629
			(43) International Publication Date: 1 May 1997 (01.05.97)
(21) International Application Number: PCT/US96/16854 (22) International Filing Date: 21 October 1996 (21.10.96) (30) Priority Data: 08/548,162 25 October 1995 (25.10.95) US (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US). (72) Inventors: LONG, Timothy, Edward; 404 Dunwoody Court, Blountville, TN 37617 (US). SPRAYBERRY, Harold, Blake; 252 Ascot Drive, Kingsport, TN 37663 (US). STAFFORD, Steven, Lee; 161 Stafford Road, Gray, TN 37615 (US). TURNER, Sam, Richard; 1037 Sussex Drive, Kingsport, TN 37660 (US). (74) Agent: HARDING, Karen, A.; P.O. Box 511, Kingsport, TN 37662-5075 (US).		(81) Designated States: AU, BR, BY, CA, CN, CZ, HU, IL, JP, KR, MX, NO, PL, RU, SG, SK, UA, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>	
(54) Title: POLYESTER/POLYAMIDE BLEND HAVING IMPROVED FLAVOR RETAINING PROPERTY AND CLARITY			
(57) Abstract <p>The present invention comprises polyester blend compositions having improved flavor retaining properties and color, comprising: (A) 98.0 to 99.95 weight percent of a polyester which comprises (1) a dicarboxylic acid component comprising repeat units from at least 85 mole percent terephthalic acid or naphthalenedicarboxylic acid derived from terephthalic acid or naphthalenedicarboxylic acid respectively; and (2) a diol component comprising repeat units from at least 85 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and (B) 2.0 to 0.05 weight percent of a polyamide; wherein the combined weights of (A) and (B) total 100 percent.</p>			

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POLYESTER/POLYAMIDE BLEND HAVING IMPROVED
FLAVOR RETAINING PROPERTY AND CLARITY

5 FIELD OF THE INVENTION

 The container market for carbonated and still
mineral water requires exceptionally low levels of
acetaldehyde (AA) in the container side wall in order to
avoid the diffusion of the AA into the water leading to
10 an undesirable water taste. AA is an inherent side
product which is generated during the polymerization
melt phase and subsequent processing steps. In
addition, variables such as catalyst selection influence
the amount of residual AA. Despite the significant
15 improvement in the PET presently produced, this level of
AA is still perceived to be too high. In fact, taste
testing has indicated that humans can taste 20 ppb
differences in AA. Consequently, there has been
significant interest in reducing the residual AA content
20 as low as possible.

 In addition to very low levels of residual AA in
the bottle sidewall, the market also demands that the
product color be as low as possible. The lack of
significant bottle sidewall color permits the use of
25 "natural" or colorless water bottles, and also
facilitates the intentional addition of dyes to generate
a desired color bottle. Bottle sidewall color is
typically reported as a b* unit which reflects the level
of yellow color in the bottle. For example, containers
30 prepared from virgin PET resin have values ranging from
0.8-1.2 b* units. Consequently, significant attention
has been devoted to the production of beverage
containers which demonstrate both low AA and low color.

 US patents 5,258,233, 5,266,413, 5,340,884 disclose
35 polyamide/PET homopolymer blends, PET/polyamide
copolymers, and PET/polyamide based concentrates.

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However, the end products have AA and/or color levels which are still undesirable for certain applications.

The use of various polyamides to increase the gas barrier properties in polyethylene terephthalate resins is disclosed in U.S. Pat. Nos. 4,837,115, 4,052,481 and 4,501,781.

U.S. Pat. No. 4,837,115 discloses a thermoplastic composition containing polyethylene terephthalate and high molecular weight polyamides which act to reduce the residual acetaldehyde contained in the polyester. U.S. Pat No. 4,837,115 states that the molecular weight of the polyamide is not critical so far as the polyamide has a film-forming property. Such polyamides, therefore, must have high enough molecular weights to form a film. It is well known in the art that polyamides having molecular weights of at least 12,000 are necessary to form a film.

SUMMARY OF THE INVENTION

The present invention comprises semi-crystalline polyester blend compositions having improved flavor retaining properties, comprising:

(A) 98.0 to 99.95 weight percent of a polyester which comprises

(1) a dicarboxylic acid component comprising repeat units from at least 85 mole percent terephthalic acid or naphthalenedicarboxylic acid derived from terephthalic acid or naphthalenedicarboxylic acid respectively; and

(2) a diol component comprising repeat units from at least 85 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and

(B) 2.0 to 0.05 weight percent of a polyamide; wherein the combined weights of (A) and (B) total 100 percent.

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The present invention further comprises a process for forming a polyester/polyamide blend comprising blending

(A) 80 to 99 weight % of a base polyester comprising

- 5 (1) a dicarboxylic acid component comprising repeat units from at least 85 mole percent aromatic dicarboxylic acid selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acid and mixtures thereof, wherein said acid is derived from terephthalic acid or naphthalenedicarboxylic acid respectively; and
- 10 (2) a diol component comprising repeat units from at least 85 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and
- 15 B) 1 to 20 weight % of a concentrate comprising:
- 1) 1 to 99 weight % of a carrier resin comprising a dicarboxylic acid component comprising repeat units from at least 60 mole percent aromatic dicarboxylic acid selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acid and mixtures thereof, and a diol component comprising repeat units from at least 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and
- 20 25 (2) 1 to 99 weight% of a polyamide which displays a melting point below the melting point of said carrier resin.
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DESCRIPTION OF THE INVENTION

This invention involves polyester/polyamide blends having surprisingly low AA and low color. By using the acid form of the acid component of the polyester instead of the ester form, the resulting polymer blends display lower AA and color than the previously produced blends. The present invention further discloses polyester/polyamide blends which are formed by mixing a polyester base resin with a concentrate containing the polyamide. The desired AA and color properties are achieved when the acid based polyesters are used as the base polymer. Preferably, both the carrier and base resins are formed from polyesters formed from the acid form of the acid component of the polyester.

The polyester (A), of the present invention is selected from polyethylene terephthalate (PET), polyethylene naphthalenedicarboxylate (PEN) or copolyesters thereof. The acid component of polyester (A) contains repeat units from at least 85 mole percent terephthalic acid, naphthalenedicarboxylic acid or mixtures thereof and at least 85 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol.

When the acid component of the polyester composition is derived from the acid form of the acid component the amount of acetaldehyde (AA) generated is less than which is typically generated when the acid component is derived from the ester form and the color is much better. Accordingly, the base is made from the acid form of the acid component (i.e. terephthalic acid and not dimethylterephthalate). Where very low AA is required preferably both the base and carrier resin are made from the acid form of polyester. It should be understood that use of the corresponding acid anhydrides

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and acid chlorides of the acids is included in the term "acid form of the polyester".

The dicarboxylic acid component of the polyester may optionally be modified with up to 15 mole percent of one or more different dicarboxylic acids. Such additional dicarboxylic acids include aromatic dicarboxylic acids preferably having 8 to 14 carbon atoms, aliphatic dicarboxylic acids preferably having 4 to 12 carbon atoms, or cycloaliphatic dicarboxylic acids preferably having 8 to 12 carbon atoms. Examples of dicarboxylic acids to be included with terephthalic acid are: phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like. Examples of dicarboxylic acids to be included with naphthalenedicarboxylic acid are: terephthalic acid, phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid, and the like. Polyesters may be prepared from two or more of the above dicarboxylic acids.

In addition, the glycol component (A)(2), may optionally be modified with up to 15 mole percent, of one or more different diols other than ethylene glycol. Such additional diols include cycloaliphatic diols preferably having 6 to 20 carbon atoms or aliphatic diols preferably having 3 to 20 carbon atoms. Examples of such diols to be included with ethylene glycol are: diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol,

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3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4),
2,2,4-trimethylpentane-diol-(1,3),
2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3),
hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene,
5 2,2-bis-(4-hydroxycyclohexyl)-propane,
2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane,
2,2-bis-(3-hydroxyethoxyphenyl)-propane, and
2,2-bis-(4-hydroxypropoxyphenyl)-propane. Polyesters
may be prepared from two or more of the above diols.

10 The resin may also contain small amounts of
trifunctional or tetrafunctional comonomers such as
trimellitic anhydride, trimethylolpropane, pyromellitic
dianhydride, pentaerythritol, and other polyester
forming polyacids or polyols generally known in the art.

15 Preferably the carrier and base resins of the
present invention should have molecular weights which
are sufficient to insure that bottles may be formed from
the resin. More preferably the resins have I.V.
(inherent viscosity, measured at 25°C using 0.5 dl/gm)
20 which are between 0.50 and 1.3 dl/gm, as determined in a
60:40 phenol:tetrachloroethane cosolvent.

The PET and PEN based polyesters of the present
invention can be prepared by conventional
polycondensation procedures well-known in the art. Such
25 processes include direct condensation of the
dicarboxylic acid(s) with the diol(s). The polyesters
may also be subjected to solid state polymerization
methods.

The second component of the present invention is a
30 polyamide capable of decreasing the AA which is
generated during the production of the base resin and
subsequent processing steps. Suitable polyamides
display a melting point below the melting point of the
polyester (PEN, PET or blends thereof). Preferably said
35 polyamide is selected from the group consisting of low

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molecular weight partially aromatic polyamides having a number average molecular weight of less than 15,000, low molecular weight aliphatic polyamides having a number average molecular weight of less than 7,000 and wholly aromatic polyamides.

Combinations of such polyamides are also included within the scope of the invention. By "partially aromatic polyamide" it is meant that the amide linkage of the partially aromatic polyamide contains at least one aromatic ring and a nonaromatic species.

The partially aromatic polyamides have an I.V. of less than 0.8 dL/g. Preferably the I.V. of the partially aromatic polyamides is less than 0.7 dL/g and the number average molecular weight is less than 12,000.

The aliphatic polyamides have an I.V. of less than 1.1 dL/g. Preferably the I.V. of the aliphatic polyamides is less than 0.8 dL/g and the number average molecular weight is less than 6,000. Wholly aromatic polyamides comprise in the molecule chain at least 70 mole % of structural units derived from m-xylylene diamine or a xylylene diamine mixture comprising m-xylylene diamine and up to 30% of p-xylylene diamine and an α -aliphatic dicarboxylic acid having 6 to 10 carbon atoms, which are further described in Japanese Patent Publications No. 1156/75, No. 5751/75, No. 5735/75 and No. 10196/75 and Japanese Patent Application Laid-Open Specification No. 29697/75.

The composition or articles of the present invention may contain up to two weight percent of the low molecular weight polyamides and preferably less than one weight percent. It has been determined that the use of polyamides at greater than two weight percent based on the weight of the polyester cause undesirable levels of haze.

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Low molecular weight polyamides formed from isophthalic acid, terephthalic acid, cyclohexanedicarboxylic acid, *meta*- or *para*-xylylene diamine, 1,3- or 1,4-cyclohexane(bis)methylamine, 5 aliphatic diacids with 6 to 12 carbon atoms, aliphatic amino acids or lactams with 6 to 12 carbon atoms, aliphatic diamines with 4 to 12 carbon atoms, and other generally known polyamide forming diacids and diamines can be used. The low molecular weight polyamides may 10 also contain small amounts of trifunctional or tetrafunctional comonomers such as trimellitic anhydride, pyromellitic dianhydride, or other polyamide forming polyacids and polyamines known in the art.

Preferred low molecular weight partially aromatic 15 polyamides include: poly(*m*-xylylene adipamide), poly(hexamethylene isophthalamide), poly(hexamethylene adipamide-co-isophthalamide), poly(hexamethylene adipamide-co-terephthalamide), and poly(hexamethylene isophthalamide-co-terephthalamide). The most preferred 20 low molecular weight partially aromatic polyamide is poly(*m*-xylylene adipamide) having a number average molecular weight of 4,000 to 7,000 and an inherent viscosity of 0.3 to 0.6 dL/g.

Preferred low molecular weight aliphatic polyamides 25 include poly(hexamethylene adipamide) and poly(caprolactam). The most preferred low molecular weight aliphatic polyamide is poly(hexamethylene adipamide) having a number average molecular weight of 3,000 to 6,000 and an inherent viscosity of 0.4 to 30 0.9 dL/g. Low molecular weight partially aromatic polyamides, are preferred over the aliphatic polyamides where clarity and dispersibility are crucial.

Preferred low molecular weight aliphatic polyamides include polycapramide (nylon 6), poly- ω -aminoheptanoic 35 acid (nylon 7), poly- ω -aminonanoic acid (nylon 9),

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polyundecane-amide (nylon 11), polyaurylactam
(nylon 12), polyethylene-adipamide (nylon 2,6),
polytetramethylene-adipamide (nylon 4,6),
polyhexamethylene-adipamide (nylon 6,6),
5 polyhexamethylene-sebacamide (nylon 6,10),
polyhexamethylene-dodecamide (nylon 6,12),
polyoctamethylene-adipamide (nylon 8,6),
polydecamethylene-adipamide (nylon 10,6),
polydodecamethylene-adipamide (nylon 12,6) and
10 polydodecamethylene-sebacamide (nylon 12,8).

The low molecular weight polyamides are generally
prepared by melt phase polymerization from a
diacid-diamine complex which may be prepared either in
situ or in a separate step. In either method, the
15 diacid and diamine are used as starting materials.
Alternatively, an ester form of the diacid may be used,
preferably the dimethyl ester. If the ester is used,
the reaction must be carried out at a relatively low
temperature, generally 80 to 120°C., until the ester is
20 converted to an amide. The mixture is then heated to
the polymerization temperature. In the case of
polycaprolactam, either caprolactam or 6-aminocaproic
acid can be used as a starting material and the
polymerization may be catalyzed by the addition of
25 adipic acid/hexamethylene diamine salt which results in
a nylon 6/66 copolymer. When the diacid-diamine complex
is used, the mixture is heated to melting and stirred
until equilibration.

The molecular weight is controlled by the
30 diacid-diamine ratio. An excess of diamine produces a
higher concentration of terminal amino groups. If the
diacid-diamine complex is prepared in a separate step,
excess diamine is added prior to the polymerization.
The polymerization can be carried out either at
35 atmospheric pressure or at elevated pressures.

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The process for preparing the polyester/polyamide blends of the present invention involve preparing the polyester and low molecular weight polyamide, respectively, by processes as mentioned previously. The polyester and polyamide are dried in an atmosphere of dried air or dried nitrogen, or under reduced pressure. The polyester and polyamide are mixed and subsequently melt compounded, for example, in a single or twin screw extruder. Melt temperatures must be at least as high as the melting point of the polyester and are typically in the range of 260-310°C. Preferably, the melt compounding temperature is maintained as low as possible within said range. After completion of the melt compounding, the extrudate is withdrawn in strand form, and recovered according to the usual way such as cutting. Instead of melt compounding, the polyester and polyamide may be dry-blended and heat-molded or draw-formed into plastic articles.

The polyamide can be added in the late stages of polyester manufacture. For example, the polyamide can be blended with the molten polyester as it is removed from the polycondensation reactor, before it is pelletized. This method, however, is not desirable if the polyester/polyamide blend will be subjected to solid state polymerization since undesirable color and/or haze may develop during extended time at elevated temperatures.

The polyamide may also be added as part of a polyolefin based nucleator concentrate where clarity is not critical such as in crystallized thermoformed articles. The polyamide may also be as a component of a polyester concentrate. The concentrate carrier resin may use either the acid or ester form of the acid component of the polyester. Preferably the carrier resin is derived from the acid form.

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Generally the concentrate comprises 1 to 99 weight % of a carrier resin comprising a dicarboxylic acid component comprising repeat units from at least 60 mole percent aromatic dicarboxylic acid selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acid and mixtures thereof, and a diol component comprising repeat units from at least 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol and 1 to 99 weight% of a polyamide described above. More preferably the carrier resin is 20 to 99 and most preferably 50 to 99 weight percent.

Generally between 1 and 20 weight percent of the concentrate is added to the base resin. More preferably 1 to 10 weight percent of the concentrate is added. It should also be understood that the base resin may contain small amounts of the ester form of the acid component, so long as the total amount of the ester form of the polyester/polyamide blend does not exceed 20 weight %, and preferably not more than 10 weight%.

The blends of this invention serve as excellent starting materials for the production of moldings of all types by extrusion or injection molding. Specific applications include various packaging applications such as thermoformed or injection molded trays, lids and cups; injection stretch blow-molded bottles, film and sheet; extrusion blow-molded bottles and multilayer articles. Examples of package contents include, but are not limited to, food, beverages, and cosmetics.

Many other ingredients can be added to the compositions of the present invention to enhance the performance properties of the blends. For example, crystallization aids, impact modifiers, surface lubricants, denesting agents, stabilizers, antioxidants, ultraviolet light absorbing agents, metal deactivators,

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colorants such as titanium dioxide and carbon black, nucleating agents such as polyethylene and polypropylene, phosphate stabilizers, fillers, and the like, can be included herein. All of these additives and the use thereof are well known in the art and do not require extensive discussions. Therefore, only a limited number will be referred to, it being understood that any of these compounds can be used so long as they do not hinder the present invention from accomplishing its objectives.

The compositions of the present invention display better color than those disclosed in US 5,258,233. Because less color is generated dyes either are not required for masking purposes or are required in lesser amounts. However, should color be desirable colorants may be added. The colorant can be added to either component of the blend during polymerization or added directly to the blend during compounding. If added during blending, the colorant can be added either in pure form or as a concentrate. The amount of a colorant depends on its absorptivity and the desired color for the particular application. A preferred colorant is 1-cyano-6-(4-(2-hydroxyethyl)anilino)-3-methyl-3H-dibenzo(F,I,J)-isoquinoline-2,7-dione used in an amount of from 2 to 15 ppm.

Desirable additives also include impact modifiers and antioxidants. Examples of typical commercially available impact modifiers well-known in the art and useful in this invention include ethylene/propylene terpolymers, styrene based block copolymers, and various acrylic core/shell type impact modifiers. The impact modifiers may be used in conventional amounts from 0.1 to 25 weight percent of the overall composition and preferably in amounts from 0.1 to 10 weight percent of the composition. Examples of typical commercially

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available antioxidants useful in this invention include, but are not limited to, hindered phenols, phosphites, diphosphites, polyphosphites, and mixtures thereof. Combinations of aromatic and aliphatic phosphite compounds may also be included.

It has been surprisingly found that by using the acid form of the acid component of the polyester and adding a polyamide, the resulting polyesters display surprisingly low AA content and good color. This was particularly surprising as the addition of polyamide is known to deleteriously effect the color of the resultant polyesters.

EXAMPLES

Preparation of polyamide

A mixture of 58.4 g (.4 mole) adipic acid and 71.5 g of distilled water were placed in a 500 mL flask, then purged 60 minutes with nitrogen. Quickly, 57.75 g m-xylylenediamine was added to the flask. The flask was equipped with an inlet for nitrogen, a metal stirrer, and a short distillation column. Then the flask was placed in a Belmont metal bath already heated to 115°C and the contents of the flask were heated at 115°C for 30 minutes. Then the temperature was raised progressively to 275°C over 25 minutes. After reaching 275°C and a clear melt, maintained 275°C for 30 minutes. A low melt viscosity, clear polyamide was obtained. Crystalline off-white on cooling. The polymer had an inherent viscosity of 0.64 (PM-95), amine endgroups of 0.13 meq/g, COOH endgroups of 0.045 meq/g, and a melting endotherm at 241°C.

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Example 1

Preparation DMT PET/polyamide concentrate.

PET 9921 derived from dimethylterephthalate (DMT) and ethylene glycol (available from Eastman Chemical Company) was dried for 6 hours at 250°F (122°C) in a tray drier. The polyamide (0.7 lb) and 14.3 lb of PET (I.V. of 0.73 dL/g.), were dry blended, extruded, and pelletized at a melt temperature of 520°F (273°C) using a Werner & Pfleiderer twin-screw extruder fitted with a 30 mm screw. Temperature settings on the extruder for the barrel and the die were 490°F (256°C) and 500°F (262°C) respectively.

Example 2

Preparation PTA PET/polyamide concentrate.

PET 9921 derived from terephthalic acid (PTA) and ethylene glycol (from Eastman Chemical Company) was dried for 6 hours at 250°F (122°C) in a tray drier. The polyamide (0.7 lb) and 14.3 lb of PET (I.V. of 0.73 dL/g.), were dry blended, extruded, and pelletized at a melt temperature of 520°F (273°C) using a Werner & Pfleiderer twin-screw extruder fitted with a 30 mm screw. Temperature settings on the extruder for the barrel and the die were 490°F (256°C) and 500°F (262°C) respectively.

Examples 3-14

The polyester compositions shown in Table 1 were injection molded on a Cincinnati Milacron preform injection molding machine under the conditions listed below.

Mold Size 1.5 l

Temperature (zones 1, 2 and nozzle) 273°C

Temperature (mold entrance) 1°C

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Pressure (psig)		Cycle (sec)	
5	Boost	860-1010	Boost 17.0
	Hold	1600	Hold 18.0
	Back	200	mold open 3.0
	Idle	0	Pst pullback 0.3
	High clamp	150	shot size 3.4
			cushion 0.25
	low clamp	75	cure 23.0

10 The injection molding machine was run with an screw speed of 80 prm and an external motor pressure of 800 psig.

15 The base resin was dried in a dehumidifying desiccant dryer at 150°C for approximately 16 hours. The concentrate was dried in smaller dryers at 100°C for approximately 16 hours. The base resin was hand blended with the concentrate at the a 50:1 base resin:concentrate ratio immediately prior to putting into the extruder hopper. The barrel was emptied of the previous material and five shots of resin were used to

20 purge the barrel before collecting samples. All samples were stored in dark plastic bags in a freezer at -20°C until submitted for testing. The preforms were stored for one-day and reheat blow molded on the a reheat blow molding machine.

25 Letdowns of the concentrate consisting of the concentrate into the base polyester resulted in the polyamide contents shown in column 4. Several preforms were made. The AA in a random preform in each blend composition shown was measured and is shown in the fifth

30 column. Bottles were blown from three random preforms in each composition and the bottle sidewall color was measured. The average bottle sidewall color is shown in the sixth column, below.

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TABLE 1

Ex. #	Base	Conc.	wt% PA	AA (ppm)	Color (b*)
	DMT	none	0	4.24	1.34
3	DMT	DMT	0.09	3.32	2.33
4	DMT	DMT	0.25	0.54	3.70
5	DMT	DMT	0.50	0.27	5.15
6	DMT	PTA	0.09	3.21	2.23
7	DMT	PTA	0.25	0.62	3.27
8	DMT	PTA	0.50	0.33	5.41
	PTA	none	0	3.67	0.99
9	PTA	PTA	0.09	2.11	1.80
10	PTA	PTA	0.25	0.57	2.57
11	PTA	PTA	0.50	0.23	3.80
12	PTA	DMT	0.09	2.59	1.45
13	PTA	DMT	0.25	0.50	3.11
14	PTA	DMT	0.50	0.29	3.97

PTA = terephthalic acid

DMT = dimethylterephthalate

The results shown in Table 1 clearly show that the polyesters made from PTA base polyester display both lower AA (except for Example 11, which is comparable) and lower color than those made from DMT base polyester. Humans can detect 20 ppb differences in AA and 0.5 differences in b*. Surprisingly, the present invention provides polyesters that display lower AA and a 5 to 35% (0.16 to 1.44) improvement in color (b*). Prior to the present invention reductions in AA came at the expense of increased color as shown by Examples 3 through 5.

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WHAT IS CLAIMED IS:

1. Polyester compositions having improved flavor retaining properties and low color, comprising:

(A) 98.0 to 99.95 weight percent of a polyester
5 which comprises

(1) a dicarboxylic acid component comprising repeat units from at least 85 mole percent aromatic dicarboxylic acid selected from the group consisting of terephthalic acid, naphthalenedicarboxylic acid and
10 mixtures thereof, wherein said acid is derived from terephthalic acid or naphthalenedicarboxylic acid respectively; and

(2) a diol component comprising repeat units from at least 85 mole percent ethylene glycol, based on 100
15 mole percent dicarboxylic acid and 100 mole percent diol; and

(B) 2.0 to 0.05 weight percent of a polyamide; wherein the combined weight percents of (A) and (B) total 100 percent.

2. The composition of claim 1 wherein said
20 polyamide is selected from the group consisting of low molecular weight partially aromatic polyamides having a number average molecular weight of less than 15,000, low molecular weight aliphatic polyamides having a number
25 average molecular weight of less than 7,000 and wholly aromatic polyamides.

3. The composition of claim 1 wherein the polyamide comprises a fully aliphatic polyamide selected from the group consisting of polycapramide (nylon 6),
30 poly- ω -aminoheptanoic acid (nylon 7), poly- ω -aminonanoic acid (nylon 9), polyundecane-amide (nylon 11), polyaurylactam (nylon 12), polyethylene-adipamide (nylon 2,6), polytetramethylene-adipamide (nylon 4,6), polyhexamethylene-adipamide (nylon 6,6),
35 polyhexamethylene-sebacamide (nylon 6,10),

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polyhexamethylene-dodecamide (nylon 6,12),
polyoctamethylene-adipamide (nylon 8,6),
polydecamethylene-adipamide (nylon 10,6),
polydodecamethylene-adipamide (nylon 12,6) and
5 polydodecamethylene-sebacamide (nylon 12,8).

4. The compositions of claim 2 wherein said partially aromatic polyamides have an I.V. of less than 0.8 dL/g.

5. The compositions of claim 2 wherein said
10 polyamide contains at least one partially aromatic polyamide having an I.V. of less than 0.7 dL/g and a number average molecular weight of less than 12,000.

6. The composition of claim 2 wherein said polyamide contains at least one aliphatic polyamide
15 having an I.V. of less than 1.1 dL/g.

7. The composition of claim 6 wherein said at least one aliphatic polyamide has an I.V. of less than 0.8 dL/g and said number average molecular weight is less than 6,000.

8. The compositions of claim 1 wherein said
20 polyamide further comprises small amounts of trifunctional or tetrafunctional comonomers selected from the group consisting of trimellitic anhydride, pyromellitic dianhydride and polyamide forming polyacids
25 and polyamines.

9. The composition of claim 1 wherein said low molecular weight partially aromatic polyamide is selected from the group consisting of poly(*m*-xylylene adipamide), poly(hexamethylene isophthalamide),
30 poly(hexamethylene adipamide-co-isophthalamide), poly(hexamethylene adipamide-co-terephthalamide), and poly(hexamethylene isophthalamide-co-terephthalamide).

10. The composition of claim 1 wherein said low molecular weight partially aromatic polyamide is
35 poly(*m*-xylylene adipamide) having a number average

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molecular weight of 4,000 to 7,000 and an inherent viscosity of 0.3 to 0.6 dL/g.

11. The composition of claim 1 wherein said polyamide comprises at least one low molecular weight aliphatic polyamide selected from poly(hexamethylene adipamide) and poly(caprolactam).

12. The composition of claim 11 wherein said polyamide comprises poly(hexamethylene adipamide) having a number average molecular weight of 3,000 to 6,000 and an inherent viscosity of 0.4 to 0.9 dL/g.

13. The composition of claim 1 wherein said dicarboxylic acid component further comprises up to 15 mole percent a second dicarboxylic acid selected from the group consisting of aromatic dicarboxylic acids having 8 to 14 carbon atoms, aliphatic dicarboxylic acids having 4 to 12 carbon atoms, cycloaliphatic dicarboxylic acids having 8 to 12 carbon atoms and mixtures thereof.

14. The composition of claim 13 wherein said dicarboxylic acid is terephthalic acid and said second dicarboxylic acid is selected from phthalic acid, isophthalic acid, 2,6-naphthalenedicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid and mixtures thereof.

15. The composition of claim 13 wherein said dicarboxylic acid is 2,6-naphthalenedicarboxylic acid and said second dicarboxylic acid is selected from terephthalic acid, phthalic acid, isophthalic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebacic acid and mixtures thereof.

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16. The composition of claim 1 wherein said glycol further comprises at least one additional diol selected from the group consisting of cycloaliphatic diols having 6 to 20 carbon atoms, aliphatic diols having 3 to 20 carbon atoms or mixtures thereof.

17. The composition of claim 16 wherein said additional diol is selected from the group consisting of diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentanediol-(2,4), 2-methylpentanediol-(1,4), 2,2,4-trimethylpentane-diol-(1,3), 2-ethylhexanediol-(1,3), 2,2-diethylpropane-diol-(1,3), hexanediol-(1,3), 1,4-di-(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethyl-cyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, 2,2-bis-(4-hydroxypropoxyphenyl)-propane and mixtures thereof.

18. The composition of claim 1 wherein up to 20 weight % of said polyester is derived from an ester form of said terephthalic acid or naphthalenedicarboxylic acid.

19. The composition of claim 1 wherein up to 10 weight % of said polyester is derived from an ester form of said terephthalic acid or naphthalenedicarboxylic acid.

20. A process for forming a blend comprising; blending

(A) 80 to 99 weight % of a base polyester comprising

(1) a dicarboxylic acid component comprising repeat units from at least 85 mole percent aromatic dicarboxylic acid selected from the group consisting of terephthalic acid,

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naphthalenedicarboxylic acid and mixtures thereof, wherein said acid is derived from terephthalic acid or naphthalenedicarboxylic acid respectively; and

- 5 (2) a diol component comprising repeat units from at least 85 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol; and
- B) 1 to 20 weight % of a concentrate comprising:
- 10 1) 1 to 99 weight % of a carrier resin comprising a dicarboxylic acid component comprising repeat units from at least 60 mole percent aromatic dicarboxylic acid selected from the
- 15 group consisting of terephthalic acid, naphthalenedicarboxylic acid and mixtures thereof, and a diol component comprising repeat units from at least 50 mole percent ethylene glycol, based on 100 mole percent dicarboxylic acid and 100 mole percent diol;
- 20 and
- (2) 1 to 99 weight% of a polyamide which displays a melting point below the melting point of said carrier resin.

21. The method of claim 20 wherein said polyamide

25 is selected from the group consisting of low molecular weight partially aromatic polyamides having a number average molecular weight of less than 15,000, low molecular weight aliphatic polyamides having a number average molecular weight of less than 7,000 and wholly

30 aromatic polyamides.

22. The method of claim 20 wherein said polyamide is selected from the group consisting of low molecular weight partially aromatic polyamides having a number average molecular weight of less than 15,000, low

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molecular weight aliphatic polyamides having a number average molecular weight of less than 7,000.

23. The method of claim 21 wherein said carrier resin dicarboxylic acid is derived from terephthalic
5 acid or naphthalenedicarboxylic acid.

INTERNATIONAL SEARCH REPORT

Intern. Appl. No.
PCT/US 96/16854

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08L67/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 258 233 (MILLS DAVID E ET AL) 2 November 1993 cited in the application see column 3, line 64 - line 65; claims 1-22	1-23
X	US,A,5 340 884 (MILLS DAVID E ET AL) 23 August 1994 cited in the application see column 4, line 18 - line 19; claims 1-10; examples 26-45	1-23
X	CH,A,684 537 (DANIEL GANZ) 14 October 1994 * complete *	1-23

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

16 January 1997

Date of mailing of the international search report

11.02.97

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/16854

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5258233	02-11-93	EP-A- 0633911 JP-T- 7509011 WO-A- 9320147 US-A- 5340884	18-01-95 05-10-95 14-10-93 23-08-94
US-A-5340884	23-08-94	US-A- 5258233 EP-A- 0633911 JP-T- 7509011 WO-A- 9320147	02-11-93 18-01-95 05-10-95 14-10-93
CH-A-684537	14-10-94	NONE	